Volume 102, Number 2, March–April 1997
Journal of Research of the National Institute of Standards and Technology

40 Years of Entropy and the Glass Transition Papers Presented at the March 1996 Meeting of the Division of High Polymer Physics of the American Physical Society

Preface

In 1956, Julian H. Gibbs published a brief but pivotal paper, "The Nature of the Glass Transition," in The Journal of Chemical Physics [J. Chem. Phys. **25**, 185 (1956)] in which he proposed a relationship between the "entropy crisis," noted by Walter Kauzmann [Chem. Rev. **43**, 219 (1948)] in 1948, and the glass transition. Kauzmann, in his only paper on glasses and supercooled liquids, made the profound observation that the configurational entropy difference between the supercooled liquid and crystalline state appears to vanish at a finite temperature in the limit of infinitely slow cooling. Six years after Kauzmann, Flory published a theory of densely packed polymers that predicted a negative configurational entropy below some finite temperature if their stiffness exceeded a critical value [Proc. Roy. Acad. Sci. **A234**, 73 (1956)]. While Flory proposed that this "crisis" would be averted by crystallization, Gibbs argued that due to their structural complexity many polymers were incapable of crystallizing, and suggested that the entropy crisis would instead be averted by a thermodynamic glass transition.

This key concept was greatly elaborated on in the subsequent papers of Gibbs and DiMarzio [J. Chem. Phys. **28**, 373 (1958); *ibid*. 807] in 1958, and by Adam and Gibbs in 1960 [J. Chem. Phys. **43**, 139 (1965)]. In recognition of the extraordinary impact on the scientific community of this series of papers by Gibbs and his coworkers, we organized a symposium "40 Years of Entropy and the Glass Transition" at the March Meeting of the American Physical Society that was held March 18–22, 1996 in St. Louis, Missouri. This Special Issue of the Journal of Research of NIST is a compilation of the symposium papers. In the first article, the theoretical underpinnings of the mobility of glass-forming liquids are given a new understanding by DiMarzio as he presents his recent efforts to relate the viscosity to the entropy in a way that goes beyond the Adam-Gibbs ansatz. Baschnagel and coworkers present results of computer simulations that support the fundamental idea that the glass transition is associated with a decrease in the entropy to some critical but nonzero value. Angell shows that the entropy paradigm has been important not only in the realm of polymer glasses, but in the inorganic glasses as well. He also discusses the entropy ideas in the context of the fragility of liquids as well as the possible relationship between polyamorphism and such biopolymer problems as "mad cow" disease.

Next, Wolynes discusses the implications of entropy for protein folding. Hodge demonstrates the usefulness of the Adam-Gibbs equations relating mobility to the configurational entropy in describing the dynamics of enthalpy recovery below the glass transition. Nagel and coworkers challenge the current view of the spin glass transition and draw analogies with the structural glass transition that suggest an underlying phase transition in structural glasses.

Finally, the contributions of both Matsuoka and Schneider include the ideas of entropy in describing experimental data for polymers as a function of such parameters as composition and molecular architecture.

As we hope the reader will agree, the papers contained in this Special Issue confirm that the ideas that sprang from the original elucidation of the relationship between entropy and the glass transition have influenced our current thinking not only about the behavior of glass-forming liquids and glassy materials, but also about such not-obviously-related phenomena as protein folding and aging in non-equilibrium glasses.

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